Best Practices in Glass Recycling

Color Modification of Post-Consumer Glass Cullet

Material: Recycled Glass

Issue: *The colors of recycled container glass - clear, green and amber - limit the applications into which it can be recycled. Methods of recolorizing recycled container glass can help to expand recycling market options, especially in high-value applications such as art glass.*

Best Practice: Recolorizing container glass can be achieved by adding chemicals to decolorize or neutralize base colors, then introducing coloring agents to achieve a new range of colors. Starting with post-consumer glass cullet, it is possible to produce a wide range of translucent colors as well as colors with controlled opacity. This Best Practice describes the results of a recolorization project. For many applications in which glass is remelted, workability and thermal compatibility are also important. Those issues, along with strategies for identifying cullet sources and making batch additions, are treated in the *Using Recycled Glass in Art Glass Applications* Best Practice.

Container glass is formulated mainly from soda ash, limestone, and silica sand (see *Chemistry of Container Glass* Best Practice). Container manufacturers produce brown glass with a sulfur-iron colloidal solution, and vary it from dark amber to honey amber with additional agents. Green bottle glass contains small amounts of chromium dissolved in the glass, with other colorants. Testing has shown that a range of colors can be achieved from color-sorted recycled container glass. However, it is important to note that the resultant colors vary widely depending on the source of glass cullet, furnace conditions, and the types of batch chemicals added. Consistency of all conditions and materials is absolutely critical. The table below summarizes some color modifications that have been made to samples of clear, green and brown cullet.

Highlights of modification potential for common container colors:

- **Brown glass** can be decolorized with the addition of zinc oxide to produce a nearly colorless glass with a blue/green hue. Erbium Oxide (Er_2O_3) and manganese oxide may be added to balance the faint blue/green hue. From this base, other colors can be produced with some of the common oxide colorants, such as cobalt, manganese, titanium, and copper. By introducing CuO with SnO_2 under reducing conditions (adding SiC reducer to the batch), a deep copper ruby was produced in test melts. By changing the time of heat treatment, the color can be struck to varying degrees of intensity.
- **Green glass** can be altered by oxidizing the melt, shifting the chrome redox equilibrium toward Cr^6+, which shifts the hue of the glass from the intense green to a yellow-green. By adding 0.5% Mn_2O_3 to the oxidized melt, the hue of the glass is neutralized, yielding a neutral smoky gray glass. Again, from this neutral base, other colors can be produced with the common oxide colorants. Densely colored, almost black, glasses can be achieved using green glass cullet.

Reagent grade or purer chemicals are best for optimal color modification. In the case of rare-earth oxides, costs may dictate choosing lower purity commercially available chemicals.

Fluxing Agents can be used to facilitate melting base glasses. Two alkali oxides were used as fluxing agents, added as water glass, 40° Be' solution of $Na_2O*3SiO_2$, and Potash (K_2C0_3). Boric oxide (B_20_3) was added as boric acid (H_3B0_3). Zinc and tin may be added as their oxides, zinc oxide (ZnO), and tin dioxide (SnO_2).

Colorants which may be added for decolorization or recolorization of base glasses include Copper added as copper (II) carbonate-dihydroxide, cobalt added as cobalt carbonate, manganese introduced as potassium permanganate, erbium oxide, neodymium oxide, cerium dioxide, and titanium dioxide. Gold may also be introduced in the form of auric chloride.

Flourine-base **opacifying agents** have been used in test melts to obtain opal colors. Phosphorus and fluorine may be added as phosphoric acid (H_3PO_4) and calcium fluoride (CaF_2). A high fluorine-content salt called PAF ($Al_3K_6F_9$), a by-product of aluminum refining, may also be used.

Opal glasses generally possess high marketability and value. However, test trials failed to produce consistent opal glasses. Flourine-based opalizing agents proved difficult to blend, and separated in the melt. This problem was exacerbated by the fact that the fluorine tended to volatilize during the melting process.

Target Color	Grape Purple	Amethyst	Honey Amber	Swimming Pool Blue	Yellow Green
Clear Cullet (%)	60.5%	63.8%	---	79.8%	71.4%
Green Cullet (%)	20.2%	21.3%	---	---	---
Brown Cullet (%)	---	---	96.3%	---	---
Melt Temp	2400°F	2420°F	2350°F	2400°F	2500°F
Work Temp	2180°F	2190°F	2250°F	2250°F	2280°F
Melt Atmosphere	Oxidation	Oxidation	Neutral	Oxidation	Neutral
Borax	16.4%	8.2%	8.2%	16.0%	6.85%
Zinc Oxide	3.0%	3.0%	0.75%	5.0%	
Potash	8.8%	8.8%		8.8%	22.1%
Manganese Dioxide	0.55%	0.385%			2.5%
Cerium Oxide	1.0%	1.0%		0.7%	
Cobalt Carbonate	0.032%	0.016%			
Sodium Nitrate	0.66%	0.462%			7.5%

All of the chemicals above require special handling for safety. Adequate ventilation is critical. **Consult Materials Safety Data Sheets for details**. Fluorine volatility represents an especially serious **health hazard,** if not appropriately managed. Water, either chemical or liquid in the batch materials, may increase the tendency of flourine to volatize. Batch adjustments should be made to balance the basic/acidic glass melt using post-consumer bottle glass.

Implementation: This information will be of use primarily to those already skilled in hot glass.

Benefits: The costs of raw materials for art glass production are significant. The information in this best practice represents potential ways that recolorization of common container glasses might be accomplished, possibly saving money for studio operators and increasing value for recyclers.

Application Sites: Glass-blowing studios and hot shops

Contact: For more information about this Best Practice, contact CWC, (206) 443-7746, e-mail info@cwc.org.

References:

Color Modification of Post-Consumer Glass Cullet, Clean Washington Center, 1996.
Dalbey, Randal, Recycled GlassWorks, Seattle, WA

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